



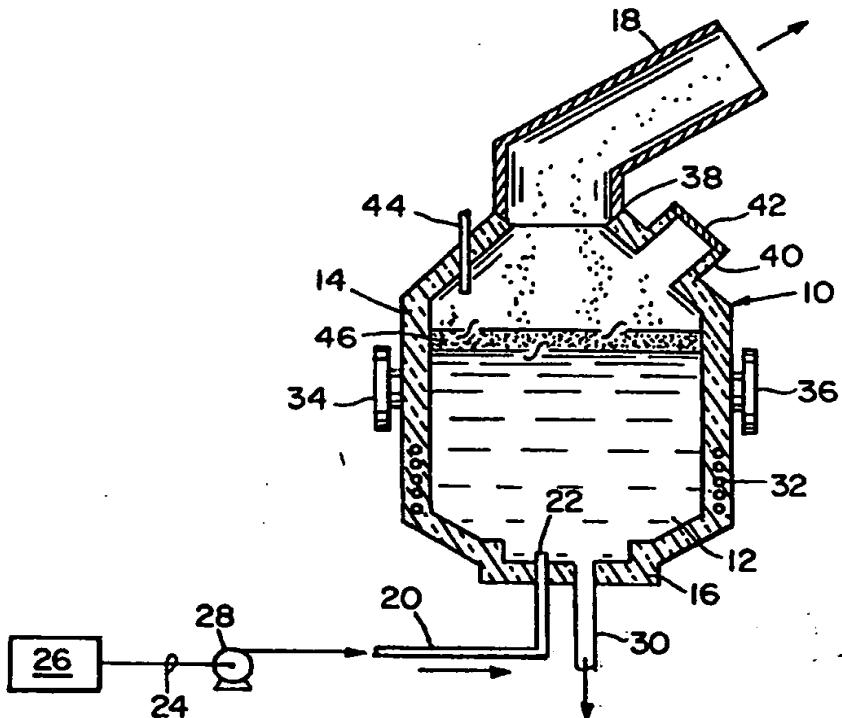
## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : <b>G01N 33/20</b>		A1	(11) International Publication Number: <b>WO 96/41161</b> (43) International Publication Date: 19 December 1996 (19.12.96)
(21) International Application Number:	PCT/US96/08454		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date:	3 June 1996 (03.06.96)		
(30) Priority Data:	08/478,461 7 June 1995 (07.06.95)	US	
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## (54) Title: MONITORING CONCENTRATION OF MOLTEN BATH COMPONENTS

## (57) Abstract

A method for monitoring concentration of components in a molten bath includes providing a molten bath wherein the bath has a known concentration of the component at a given feed rate of a feed into the molten bath. For example, methane and hydrogen gas concentrations can be measured in off-gas released by a molten metal bath. The measured amounts of the methane and hydrogen gas can be correlated with known amounts of methane and hydrogen gas for a given concentration of carbon in the molten metal bath at steady state conditions, thereby monitoring the concentration of carbon in the molten metal bath.



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-1-

MONITORING CONCENTRATION OF MOLTEN BATH COMPONENTS

Background of the Invention

Disposal of organic wastes in landfills and by incineration has become an increasingly difficult problem 5 because of diminishing availability of disposal space, strengthened governmental regulations, and the growing public awareness of the impact of hazardous substance contamination upon the environment. Release of hazardous organic wastes to the environment can contaminate air and 10 water supplies, thereby diminishing the quality of life in the affected populations.

To minimize the environmental effects of the disposal of organic wastes, methods must be developed to convert these wastes into benign, and preferably, useful 15 substances. In response to this need, there has been a substantial investment in the development of alternate methods for suitably treating hazardous organic wastes. One of the most promising new methods is described in U.S. Patents 4,574,714 and 4,602,574, issued to Bach and Nagel. 20 The Bach/Nagel method for destroying organic material, including toxic wastes, involves decomposition of the organic material to its atomic constituents in a molten bath and reformation of these atomic constituents into environmentally acceptable products.

25 Operation of systems which employ molten baths for treatment of hazardous organic wastes can require continuous or intermittent monitoring of process parameters, such as carbon concentration of the molten baths. Typically, the concentration of carbon in a molten 30 bath requires that the bath be sampled. The sampled portion of the bath is then generally cooled and analyzed

-2-

to determine the carbon concentration. This method is generally very time consuming and, consequently, is of limited utility to monitor the status of a molten bath during processing of hazardous organic wastes.

5 Therefore, a need exists for a method to monitor the concentration of carbon in molten baths which eliminates or minimizes the above-referenced problems.

#### Summary of the Invention

10 This invention relates to a method for monitoring the concentration of a compound of a molten bath.

The method includes providing a molten bath, the molten bath having a known concentration of the component at a given feed rate of material, that includes the component, into the molten bath. The content of the 15 component is measured in the off-gas released by the molten bath, whereby said measured content can be correlated with known amounts of said component for a given concentration of the component in the molten bath at steady state conditions, thereby monitoring the concentration of the 20 component in the molten bath.

In a specific embodiment, the method includes providing a molten bath, the molten metal bath having a known concentration of carbon at a given feed rate of an organic-containing feed into the molten metal bath. The 25 content of methane and hydrogen gas in off-gas released by the molten metal bath is measured, whereby the measured amounts of the methane and hydrogen gas can be correlated with known amounts of methane and hydrogen gas for a given concentration of carbon in the molten bath at steady state 30 conditions, thereby monitoring the concentration of carbon in the molten metal bath.

This invention has the advantage, for example, of enabling estimation of the concentration of a component, such as carbon, of a molten bath without having to sample

-3-

the bath. Consequently, equipment typically required to extract samples from molten baths is rendered unnecessary. Further, analysis of component concentration can be made within a relatively short period of time because certain 5 process steps, such as cooling of a sample removed from the molten bath, and subsequent processing of the sample, are eliminated by the method of the invention. Also, the determination of component concentration can be made continuously. In addition, the accuracy of the 10 measurement, relative to measurement of an extracted sample, can be significantly increased because sampled gas flow more accurately reflects the overall composition of a typical molten bath than would a small sample taken from one portion of the molten bath. In addition, the accuracy 15 of measurement can be significantly increased in certain circumstances by injecting a component, such as hydrogen gas or hydrocarbon feed, into an isolated portion of the bath, and subsequently sampling gas discharged from the bath at a point proximate to the point of injection of the 20 feed.

#### Brief Description of the Drawing

The Figure shows a cross section of an embodiment in a molten bath which is suitable for use by the method of the invention.

#### 25 Detailed Description of the Invention

The features and other details of the method of the invention will now be more particularly described with reference to the accompanying drawing and pointed out in the claims. It will be understood that the particular 30 embodiments of the invention are shown by way of illustration and not as limitations of the invention. The principle features of this invention can be employed in

-4-

various embodiments without departing from the scope of the invention.

The present invention generally relates to a method for monitoring concentration of a component of a molten bath. This invention is an improvement of the Bach/Nagel method disclosed in U.S. Patents 4,574,714 and 4,602,574, the teachings of which are incorporated by reference in their entirety. The teachings of U.S. Serial Nos. 07/895,358 and 07/895,346 are also incorporated by reference in their entirety.

One embodiment of apparatus suitable for employment of the invention is illustrated in the Figure. Therein, reactor 10 includes molten bath 12. Examples of suitable reactors include appropriately modified steel making vessels known in the art as K-BOP, Q-BOP, argon-oxygen decarbonization furnaces (AOD), BOF, etc. Reactor 12 includes upper portion 14 and lower portion 16. Off-gas outlet 18 extends from upper portion 14 and is suitable for conducting an off-gas composition out of reactor 10.

Material inlet tube 20 includes material inlet 22 and extends from lower portion 16 of reactor 10. Line 24 extends between material source 26 and material inlet tube 20. Pump 28 is disposed at line 24 for directing material from material source 26 through organic material inlet tube 20 and into molten bath 12 contained in reactor 10.

It is to be understood, however, that more than one material tube can be disposed at lower portion 16 of reactor 10 for introduction of material into reactor 10. Other means, such as an injection lance (not shown), can also be employed to introduce material into molten bath 12 in reactor 10.

Bottom tapping spout 30 extends from lower portion of reactor 10 and is suitable for removal of at least a portion of molten bath 12 from reactor 10. Induction coil 32 is disposed at lower portion 16 for heating molten bath

-5-

12 in reactor 10. It is to be understood that, alternatively, reactor 10 can be heated by other suitable means, such as by oxyfuel burners, electric arcs, etc.

Trunions 34, 36 are disposed at reactor 12 for 5 manipulation of reactor 10. Seal 38 is disposed between off-gas outlet 18 and is suitable for allowing partial rotation of reactor 10 about trunions 34, 36 without breaking seal 38. Reactor 10 is sealed at port 40 by lid 42. Gas probe 44 extends into reactor 10 at upper portion 10 14. Gas probe 44 is suitable for removing samples of gas from above molten bath 12 and/or analyzing the concentration of gas components in off-gas discharged by molten bath 12.

Examples of suitable components of molten bath 12 15 include iron, copper, chromium and manganese. Molten bath 12 can include more than one metal. For example, molten bath 12 can include a solution of miscible metals, such as iron and chromium. It is to be understood that, alternatively, molten bath 12 can be a molten salt bath.

20 Suitable metals are those with melting points within the operating conditions of the system. It is preferred, for example, to operate molten bath 12 at a temperature in a range of between about 1,300°C and 1,700°C.

In one embodiment, where the component to be measured 25 is carbon, and molten bath 12 is a molten metal bath, suitable metals are typically those that have a carbon solubility which is sufficient to allow significant amounts of hydrogen to be generated, as the feed, such as an organic waste, is decomposed and the molten metal becomes 30 carbonized. Thus, metals with a carbon solubility of greater than about 0.5%, by weight, are suitable, and those with a carbon solubility of greater than about two percent, by weight, are particularly suitable. In the cases where more than one metal is employed, at least one of the metals 35 should have the aforementioned carbon solubility.

-6-

In many cases, it is preferred to have the viscosity of the molten metal in reactor less than about 10 centipoise at the operating conditions of reactor.

Molten bath 12 can be formed by at least partially filling reactor 10 with a suitable metal. The metal is then heated to a suitable temperature by activation of induction coil 32 or by some other suitable means, not shown. Suitable operating conditions of the system include a temperature sufficient to at least partially convert organic material by thermal decomposition. Generally, a temperature in the range of between about 1,300° and about 1,700°C is suitable.

Optionally, molten bath 12 can have vitreous or slag layer 46 disposed thereon. Vitreous layer 46 is substantially immiscible with molten bath 12. Vitreous layer 46 can have a lower thermal conductivity than that of molten bath 12. Radiant heat loss from molten bath 12 can thereby be reduced to significantly below the radiant heat loss from molten bath 12 where no vitreous layer is present.

A wide variety of feed materials are suitable for treatment by this invention. An example of a suitable feed material is an organic waste, such as a hydrogen-containing carbonaceous material, including oil or a waste which includes organic compounds containing nitrogen, sulfur, oxygen, etc. It is to be understood that the organic material can include inorganic compounds. In addition to carbon and hydrogen, the organic waste can include other atomic constituents, such as halogens, metals, etc. The organic waste does not need to be anhydrous. However, significant amounts of water in the organic waste can cause the water to act as an oxidizing agent, thereby interfering with the formation of hydrogen gas. For the production of a greater yield of hydrogen gas, a preferred organic waste

-7-

includes a relatively high hydrogen containing carbonaceous material, such as propane, butane, etc.

Other suitable feed materials include those which include any of the following components, the concentrations 5 of which would be monitored in molten bath 12: arsenic (As); barium (Ba); cadmium (Cd); chromium (Cr); lead (Pb); mercury (Hg); selenium (Se); silver (Ag); antimony (Sb); halogens, such as chlorine, hydrogen; sulfur; oxygen; etc.

Feed material is directed from material source 26 10 through line 24 by pump 28 and is injected into molten bath 12 through material inlet tube 20. In one embodiment, the material is a fluid which can include materials which are dissolved or suspended within a liquid. In another embodiment, solid particles are suspended in an inert gas, 15 such as argon.

Feed material directed into molten bath 12 can be converted to its atomic constituents, such as carbon and hydrogen. Where hydrocarbons are directed into molten bath 12, the atomic hydrogen is then formed into hydrogen gas in 20 the absence of an oxidizing agent and molten bath 12 is concurrently carbonized. The term, "carbonized," as used herein, means the addition of atomic carbon to molten bath 12 to increase the overall quantity of carbon contained in molten bath 12 without any substantial losses of carbon 25 from molten bath 12 due to oxidation by a separately added oxidizing agent.

Hydrogen gas migrates through molten bath 12 by diffusion, bubbling or other means. At least a portion of the hydrogen gas migrates to a portion of molten bath 12 30 proximate to off-gas outlet 18 to form a hydrogen gas stream. The hydrogen gas stream can be an enriched hydrogen gas stream. An enriched hydrogen gas stream, as that term is used herein, means a gas stream wherein the molar fraction of hydrogen contained in the gas stream, 35 based upon the total hydrogen and carbon oxide in the gas

-8-

stream, is greater than that generally produced in a typical process disclosed by Bach/Nagel in U.S. Patents 4,574,714 and 4,602,574 for the simultaneous, combined decomposition and oxidation of an organic material. The 5 molar fraction of hydrogen is the ratio of the moles of hydrogen contained in a gas stream to the sum of moles of hydrogen and moles of carbon oxide gases contained in the gas stream.

The concentration of the dissolved component to be 10 monitored in molten bath 12 is preferably limited to an amount below its saturation point at the temperature of molten bath 12. Thus, for iron, the concentration of atomic carbon is generally limited to a concentration of less than about five percent, by weight, at 1,800°C. Where 15 the molten metal is cobalt, the saturation point of carbon is in the range of between about three percent at 1,400°C and about 4.3 percent, by weight at 1,800°C. Similarly, for manganese, the saturation point of carbon is in the range of between about eight percent at 1,400°C and about 20 8.5 percent, by weight, at 1,800°C. For chromium, the saturation point of carbon is in the range of between about eleven percent at 1,800°C and about fifteen percent, by weight, at 2,000°C.

The method of the invention includes providing a 25 molten bath 12 wherein molten bath 12 has a known concentration of the component to be monitored at a given feed rate of a feed material, such as a hydrocarbon, into molten bath 12. The concentration of the monitored compound in molten bath 12 at a given feed rate of an feed 30 material is determined by establishing steady state conditions in molten bath 12 at that feed rate of the material. A sample of the bath is removed by a conventional method and analyzed for the component content.

While maintaining steady state conditions in molten 35 bath 12, off-gas released by molten bath 12 is analyzed by

-9-

employing gas probe 44 to determine the concentration of the component in the off-gas. Once molten bath 12 and the off-gas have been sampled, the rate of injection of the feed material into molten bath 12 is changed and steady 5 state conditions are reestablished in molten bath 12. Molten bath 12 and the off-gas are again sampled and analyzed for content of the monitored component in the bath sample, and for the component, or corresponding compounds, in the off-gas sample.

10 For example, at a given temperature, measurement of carbon concentration in molten bath 12, and of methane and hydrogen gas concentration in the off-gas, at various hydrocarbon feed rates, establishes a calibration curve. Subsequent determination of methane and/or hydrogen gas 15 concentration in the off-gas at that temperature, and at approximately steady state conditions, can be employed, using the calibration curves, to determine the carbon concentration of molten bath 12. The carbon concentration of molten bath 12 can thereby be monitored without 20 requiring extraction of a sample of the bath for analysis. Further, the methane and hydrogen gas concentrations in the off-gas can be monitored continuously, or intermittently, thereby providing, in conjunction with the calibration curves, a rapid assessment of the carbon concentration in 25 molten bath 12 at any given time. Examples of other forms in which the component can be measured in the off-gas include: the elemental form of the component; an oxide of the component; a sulfide of the component; a halide of the component, such as a chloride of the component, including, 30 for example, hydrochloric acid; etc. Specific compounds that can be measured in the off-gas include: methane; carbon monoxide; methylene chloride; hydrogen gas; sulfur oxides; chlorine gas; etc.

-10-

Calibration curves can also be established for the same bath at different temperatures, and employing different molten baths.

Optionally, a feed material can be injected into 5 molten bath 12 at an injection point which is remote from the point of injection at the bulk of the feed to be treated. Gas discharged from molten bath 12 at a point proximate to the submerged injection point of the feed can be sampled for analysis of gas content.

10 Equivalents

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to specific embodiments of the invention described specifically herein. Such equivalents are 15 intended to be encompassed in the scope of the following claims.

-11-

CLAIMS

We claim:

1. A method for monitoring carbon concentration in a molten bath, comprising the steps of:
  - 5 a) providing a molten bath, said molten bath having a known concentration of carbon at a given feed rate of an organic-containing material into the molten bath;
  - b) measuring methane and hydrogen gas content of off-gas released by said molten bath, whereby said measurements of the methane and hydrogen gas can be correlated with known amounts of methane and hydrogen gas for a given concentration of carbon in the molten bath at steady state conditions, thereby monitoring the concentration of carbon in the molten bath.
- 10 2. The method of Claim 1, further including the steps of:
  - a) injecting an organic-containing feed into the molten bath at a submerged injection point;
  - 20 b) sampling gas discharged from the bath at a point proximate to said submerged injection point; and
  - c) measuring the methane concentration of said sampled gas.
- 25 3. The method of Claim 1, further including the steps of:
  - a) injecting a hydrogen gas feed into the molten bath at a submerged injection point;
  - b) sampling gas discharged from the bath at a point proximate to said submerged injection point; and
  - c) measuring the methane concentration of said sampled gas.
- 30

-12-

4. The method of Claim 3, further including the step of measuring the hydrogen gas content of the sampled gas.
5. A method for monitoring concentration of a component of a molten bath, comprising the steps of:
  - 5 a) providing a molten bath, said molten bath having a known concentration of said component at a given feed rate of a material, that includes said component, into the molten bath; and
  - 5 b) measuring a content of the component in off-gas released by the molten bath, whereby said measured content can be correlated with known amounts of said component for a given concentration of the component in the molten bath at steady state conditions, thereby monitoring the concentration of the component in the molten bath.
- 10 6. A method of Claim 5 wherein the component is selected from the group consisting of arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver and antimony.
- 15 7. A method of Claim 6 wherein the component is measured in the form of an oxide compound of the component.
- 20 8. The method of Claim 6 wherein the component is measured in the form of a sulfide compound of the material.
- 25 9. The method of Claim 6 wherein the component is measured in the form of a halide compound of the component.

-13-

10. The method of Claim 9 wherein the halide compound includes chlorine.
11. The method of Claim 6 wherein the amount of the component is measured while the component is in elemental form.
12. The method of Claim 5 wherein the component is arsenic.
13. The method of Claim 5 wherein the component is barium.
14. The method of Claim 5 wherein the component is cadmium.
15. The method of Claim 5 wherein the component is chromium.
16. The method of Claim 5 wherein the component is lead.
17. The method of Claim 5 wherein the component is mercury.
18. The method of Claim 5 wherein the component is selenium.
19. The method of Claim 5 wherein the component is silver.
20. The method of Claim 5 wherein the component is antimony.
21. The method of Claim 5 wherein the molten bath is a molten metal bath.

-14-

22. The method of Claim 21 wherein the molten bath includes copper.
23. The method of Claim 22 wherein the component includes sulphur.
- 5 24. The method of Claim 23 wherein the amount of the sulphur is measured while the sulphur is in the form of an oxide.
25. The method of Claim 22 wherein the component includes carbon.
- 10 26. The method of Claim 25 wherein the amount of the carbon is measured while the carbon is in the form of an oxide.
27. The method of Claim 26 wherein the carbon oxide is carbon monoxide.
- 15 28. The method of Claim 25 wherein the amount of carbon is measured while the carbon is in the form of a hydrocarbon.
29. The method of Claim 28 wherein the hydrocarbon is methane.
- 20 30. The method of Claim 25 wherein the amount of carbon is measured while the carbon is in the form of methylene chloride.
31. The method of Claim 21 wherein the component includes a halogen.

-15-

32. The method of Claim 21 wherein the halogen is chlorine.
33. The method of Claim 31 wherein the amount of the halogen is measured while it is in the form of a halogenated compound.
- 5 34. The method of Claim 32 wherein the halogenated compound is a halogenated hydrocarbon.
35. The method of Claim 33 wherein the halogenated compound is methylene chloride.
- 10 36. The method of Claim 31 wherein the amount of the halogen is measured while it is in the form of a gaseous halogen.
37. The method of Claim 35 wherein the gaseous halogen is chlorine gas.
- 15 38. The method of Claim 31 wherein the amount of the halogen is measured while it is in the form of an acid.
39. The method of Claim 37 wherein the acid is hydrochloric acid.
- 20 40. The method of Claim 21 wherein the molten bath includes iron.
41. The method of Claim 40 wherein the component includes sulphur.

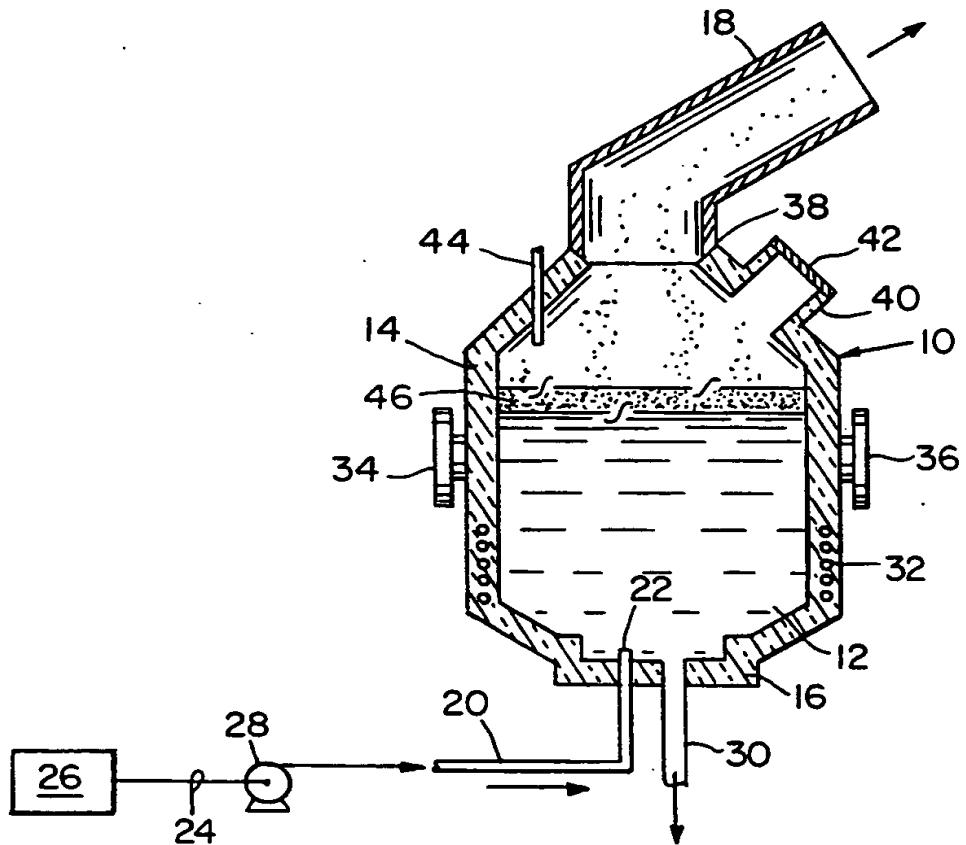
-16-

42. The method of Claim 41 wherein the amount of the sulphur is measured while the sulphur is in the form of an oxide.
43. The method of Claim 40 wherein the component includes carbon.
44. The method of Claim 43 wherein the amount of the carbon is measured while the carbon is in the form of an oxide.
45. The method of Claim 44 wherein the carbon oxide is carbon monoxide.
46. The method of Claim 43 wherein the amount of carbon is measured while the carbon is in the form of a hydrocarbon.
47. The method of Claim 46 wherein the hydrocarbon is methane.
48. The method of Claim 43 wherein the amount of carbon is measured while the carbon is in the form of methylene chloride.
49. The method of Claim 21 wherein the component includes a halogen.
50. The method of Claim 49 wherein the halogen is chlorine.
51. The method of Claim 49 wherein the amount of the halogen is measured while it is in the form of a halogenated compound.

-17-

52. The method of Claim 51 wherein the halogenated compound is a halogenated hydrocarbon.
53. The method of Claim 52 wherein the halogenated compound is methylene chloride.
- 5 54. The method of Claim 49 wherein the amount of the halogen is measured while it is in the form of a gaseous halogen.
55. The method of Claim 54 wherein the gaseous halogen is chlorine gas.
- 10 56. The method of Claim 49 wherein the amount of the halogen is measured while it is in the form of an acid.
57. The method of Claim 56 wherein the acid is hydrochloric acid.
- 15 58. The method of Claim 5 wherein the molten bath is a molten salt bath.

1/1



## INTERNATIONAL SEARCH REPORT

Int'l Application No  
PCT/US 96/08454A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 G01N33/20

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO,A,86 02847 (USS ENGINEERS AND CONSULTANTS, INC.) 22 May 1986 cited in the application see the whole document & US,A,4 602 574 & US,A,4 574 714 ---	1,5
A	DE,A,15 83 297 (UNITED STATES STEEL CORP.) 30 July 1970 see page 8, paragraph 3 - page 20, paragraph 2 ---	1,5

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Date of the actual completion of the international search  11 September 1996	Date of mailing of the international search report  26.09.96
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## INTERNATIONAL SEARCH REPORT

Int'l Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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